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Oily sludge catalytic pyrolysis combined with fine particle removal using a Ni-ceramic membrane

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Abstract

Pyrolysis is one of the effective technology for oily sludge treatment and energy recovery. However, pyrolysis of oily sludge generates solid particles which are taken away from the reactor by gas, causing blockage in downstream equipment and reducing the quality of pyrolysis oil and gas. A study on the clean catalytic pyrolysis of oily sludge was carried out, by incorporating a ceramic membrane with or without Ni inside the pyrolysis reactor. It aims to investigate the effect of ceramic membrane on oily sludge pyrolysis and particulate removal. The yield of the pyrolysis gas produced from the reaction with Ni-ceramic membrane is 31.46 L/kg, while the recovery rate of pyrolysis oil is 48.21%. On the contrary, the yield of the pyrolysis gas produced from the reaction with blank ceramic membrane is 17.92 L/kg, while the recovery rate of pyrolysis oil is 62.63%. The particulate matter content in gas without and with Ni-ceramic membrane are 2.74 and 0.07 mg/L. The particulate matter content in oil without and with Ni-ceramic membrane are 3708.9 and 156.7 mg/L, respectively. Results indicated that the Ni catalyst loading on the ceramic membrane could improve the yield of the pyrolysis gas and remove the fine particles effectively. In addition, a long-time catalytic pyrolysis experiment was carried out, with the feeding speed of 4.17 g/min and the reaction temperature of 500 ^{o}C. It was found from the set conditions that the Ni-ceramic membrane could be

used continuously for 420 min.

Key words: Oily sludge; Catalytic pyrolysis; Ni-ceramic membrane; Particulate matter

1. Introduction

The operations of crude oil exploration, production, transportation, storage and refining can generate a great deal of oily sludge in petroleum industry [1]. Oily sludge is a complex semi-solid mixture which consists of water, various petroleum hydrocarbons, solid material and metals. Oily sludge is considered as hazardous waste in many countries due to its hazardous nature [2]. The serious threats to the environment and human health was posed with insufficient disposal or treatment of oily sludge [3]. Therefore, the effective recovery and utilization method of oily sludge has attracted a growing attention in recent years.

Pyrolysis is a method of thermal decomposition of organic materials at high temperature in an inert environment [4]. The pyrolysis process of oily sludge produces solid product (chars), condensable hydrocarbons (oil) and non-condensable gases. The recovered oil could be used as fuels or sources of other valuable chemical products [5]. Furthermore, pyrolysis gas and char can be used to provide heat and generate electricity [6]. Several studies have been reported to use pyrolysis for fuel recovery from oily sludge. Qin et al [7] studied the pyrolysis of oily sludge in a fluidized bed reactor. The results demonstrated that the maximum oil yield (59.20%) was achieved at 500 °C and the simultaneous recovery of oil and iron from oily sludge by pyrolysis was feasible. Schmidt et al [8] pointed out that about 70-84% of oil could be recycled from oily sludge during pyrolysis at a temperature range of 460-650 ^{o}C in a fluidized bed reactor. The pyrolysis oil was close to the diesel oil, however, abundant heavy components (such as asphaltene and gelatin) severely affect the quality of oil products [9].

Pyrolysis of oily sludge generates solid fine particles which are removed from the reactor by carrier gas. These particles can cause fouling and blockage of downstream equipment. Furthermore, the quality of pyrolysis oil and gas are reduced and are not suitable to be used as alternative fuels due to the existence of large number of solid particles in oil and gas. Therefore, it is necessary to find an effective method to remove particles from oil and gas to obtain high quality products. However, obstacles exist to restrict development of particle removal technology. The removal of particles from oil and gas products respectively will increase the processing cost obviously. In addition, it is difficult to remove particles from the pyrolysis oil under room temperature. To solve these problems, a high temperature filtration unit can be used to reduce the particles from high temperature gas before it condenses into oil. In this way, the particles in pyrolysis oil and pyrolysis gas can be removed simultaneously.

Furthermore, useful catalysts were added during the pyrolysis process to improve the quality of oil products. The catalytic cracking methods are feasible in lowering reaction temperature, shortening reaction time and changing product distribution [10]. Vast amount of studies on the addition of catalysts to the oily sludge during the pyrolysis process have been conducted. A variety of catalysts have been widely used for the oily sludge pyrolysis, such as aluminum compounds (Al, Al_2O_3 and $AlCl_3$), iron compounds (Fe, Fe_2O_3, $FeCl_3$ and $FeSO_4 \cdot 7H_2O$), calcium compounds (CaO, $Ca(OH)_2$, $CaCl_2$ and $CaCO_3$), Ni-based catalysts, Co-based catalysts, KOH, dolomite and olivine [11-15]. Lin et al [11] suggested that quality of pyrolysis oil was improved due to the addition of KOH according to smaller average molecular weight, lower viscosity, higher heating value, less asphaltenes and more straight chain hydrocarbons.

Nowadays, the research focus in pyrolysis of oily sludge is to develop new catalyst with high performance. Ni-based catalysts have shown an excellent advantage in the pyrolysis and gasification reaction, with an activity comparable to noble metal catalysts [16-18]. The catalytic activity is related to the carriers' property, active phase precursor, synthesis and pretreatment method [19, 20]. The supporting material is considered as the key role in the performance of the Ni-based catalyst. Ceramic membrane is a porous material with high porosity. Ceramic membranes have some advantages such as high chemical, mechanical, thermal resistance and low price [21, 22]. Due to the good physical properties of ceramic membrane, it can be used as Ni-based catalyst carrier for oily sludge pyrolysis to improve the quality of products. So far, there are few studies on the ceramic membrane as active core to support nickel for oily sludge pyrolysis.

Furthermore, our previous research results suggested that the ceramic membrane can remove particulate matter from the pyrolysis gas [23]. In order to improve the quality of pyrolysis products and remove particulate matter at the same time, tubular ceramic membrane was selected as the catalyst carrier. Therefore, the Ni-ceramic membrane catalyst was prepared in this study. Moreover, the clean catalytic pyrolysis of oil sludge was carried out by incorporating a tubular ceramic membrane inside the pyrolysis reactor for the pyrolysis of oily sludge, aiming to significantly enhance the removal of particles from the pyrolysis gas and the improvement of product quality.

2. Experimental section

2.1 Materials

The oily sludge was selected as raw material from Shaanxi Yanchang Petroleum Group in China. Proximate analysis was performed with a muffle furnace (Yamato FO410C, Japan) according to the standard method (GB/T 212-2008). C, H, N and S analysis of oily sludge was obtained with an Elementar Vaeeio MACRO elemental analyzer. The estimation content of O is carried out by subtracting the sum of other compositions (ash, C, H, N and S) from 100%. Table 1 shows the proximate and ultimate analysis results, oil content and HHV of oily sludge. The result indicates the oily sludge of low moisture, moderate volatile matter, high ash and very low fixed carbon content. Soxhlet extraction was used to measure the oil content of oily sludge, which was 17.89%. The calorific value was measured with a bomb calorimeter (Sande SDC-5015, China) with 8.12 MJ /kg.

Table 1 Properties of oily sludge sample

Proximate analysis[a] (wt%)				Ultimate analysis[b] (wt%)					Oil content (wt%)	HHV （MJ/kg）
M	V	A	FC	C	H	O[c]	N	S		
10.64	21.03	65.27	3.06	70.13	11.85	8.72	3.43	5.87	17.89	8.12

[a] On received basis. [b] On ash-free basis. [c] By difference.

Thermogravimetric (TG) analysis was carried out using a thermogravimetric analyzer (Shimadzu TG-DSC STA449F3, Japan). Nitrogen was used as purge gas, and the flow rate was 75 ml/min. 10-15 mg of oily sludge samples were heated from room temperature to 900 ^{o}C at heating rates of 5, 10, 15 and 20 ^{o}C/min under nitrogen atmosphere to test the effect of heating rates on pyrolysis.

2.2 Catalyst preparation

Impregnation method was employed to prepare Ni-ceramic membrane (Ni-CM) catalyst. The specific amount of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water to obtain 1 mol/L $Ni(NO_3)_2$ solution. The clean ceramic membrane was dipped into the $Ni(NO_3)_2$ solution for 12h, and then the derived catalyst precursor was dried in an oven for 12h at 105 ºC. The precursor was calcined under air atmosphere at 700 ºC for 2h in a reactor, followed by reduction at 500 ºC for 2h within mixture of nitrogen and hydrogen, for N_2/H_2 volume ratio of 4:1.

The total amount of Ni loading on Ni-ceramic membrane (Ni-CM) catalyst was calculated by using the following equation:

$$M_{CM} = \frac{M_{CM-1} - M_{CM-0}}{M_{CM-0}} \times 100\% \quad (1)$$

where, M_{CM} is the total amount of Ni loading on catalyst; $M_{CM\text{-}1}$ is the weight of Ni-ceramic membrane catalyst, g; $M_{CM\text{-}0}$ is the weight of clean ceramic membrane, g.

The total amount of Ni loading on each Ni-CM catalyst was controlled to be around 1.03%.

2.3 Catalyst characterization

Scanning electron microscopy and backscattered electron imaging (SEM/BSE, JEOL 7800F, Japan) were carry out to detect the microstructure of blank ceramic membrane, fresh Ni-CM and used Ni-CM catalyst, and distribution of different elements. Energy dispersive spectrometer (EDS) was used to measure content of the surface components. The association of catalysts was performed by using X-ray diffractometer (XRD, PANalytical XPertPRO, Netherlands). The range of 2 theta angle was changed from 10 to 95° with a scanning step of 4°/min. The X-ray fluorescence spectrometer (XRF, PANalytical Axios PW4400, Netherlands) was used to determine the elements of catalysts.

2.4 Experimental

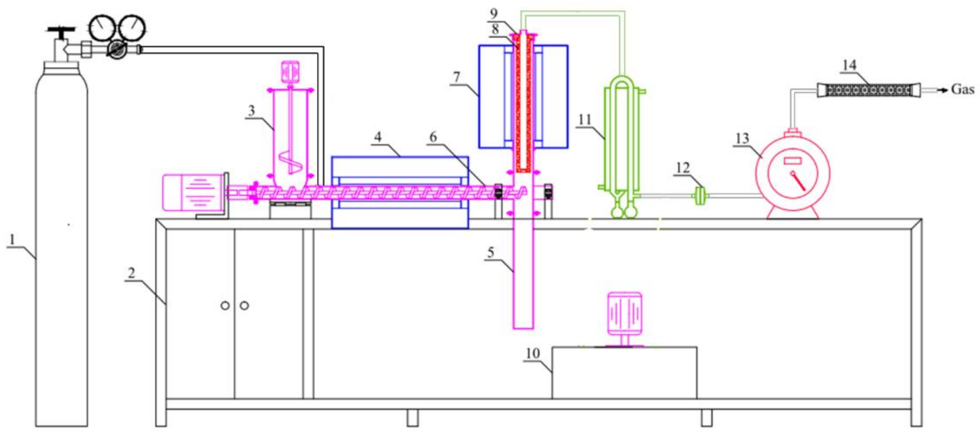

Figure 1. Schematic of oily sludge spiral pyrolysis apparatus

1. Nitrogen cylinder; 2. Control cabinet; 3. Feeding bin; 4. Tubular furnace A; 5. Residue collector; 6. Pyrolysis reactor; 7. Tubular furnace B; 8. Ceramic membrane; 9. Catalytic filter reactor; 10.

Cooling water; 11. Condenser; 12. Gas particle filter; 13. Wet gas meter; 14. Desiccator

The clean pyrolysis of oily sludge was carried out in a self-fabricated spiral continuous reactor, which is shown in Figure 1. This device consists of a pyrolysis reactor with a spiral screw, a catalytic filter reactor with a blank CM or a Ni-CM, an electrical heating system, a residue collector, a condensing system and a gas product collection system. The temperatures of pyrolysis reactor, catalytic filter reactor and residue collector were controlled by temperature regulator and K-type thermocouples.

The oily sludge was placed in the feeding bin before each experiment. Then, N_2 with the flow rate of 200 mL/min was injected into the reactor to ensure an oxygen-free system. When the reactor temperature reached the required value (500 ºC), the oily sludge was fed to the reactor at a desired feeding rate. The volatiles were fed into the catalytic filter reactor that fixes a Ni-CM catalyst. When volatiles went through the Ni-CM catalyst, particulate matter entrained into the volatiles can be trapped by the Ni-CM. The gas was reformed in the catalytic filter reactor and introduced to the condensing system. The liquid product was separated and collected in a liquid tank. Meanwhile, gas product passed through the gas particle filter, and the volume of gas was confirmed by a wet flowmeter and dried by passing through a silica-gel drier. The pyrolysis gas was collected by a gas collection bag. The numerical difference of wet flowmeter is the volume of pyrolysis gas generated during the pyrolysis process. The pyrolysis residue was collected by residue collector and weighed after the spiral pyrolysis apparatus cooled to room temperature. All experiments were repeated 3 times to obtain the accurate experimental data.

To evaluate the removal effect of ceramic membrane on particulate matter and catalytic effect of Ni-CM on oily sludge pyrolysis, three contrast experiments with no CM (E1), blank CM (E2) and

Ni-CM catalyst (E3) in the catalytic filter reactor were performed at same operational conditions (i.e. temperature of 500 ^{o}C, feeding speed of 4.17 g/min and reaction time of 2h).

2.5 Product analyses

2.5.1 Pyrolysis oil and gas analyses

The composition of the gas was analyzed off-line by a China Tianmei 7900 gas chromatograph (GC) with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Nitrogen was used as a tracer of GC to quantify the volume percent of each gas product. The yields of oil and char were estimated based on the weight of each product.

The high heating value (HHV) of oils was conducted by a bomb calorimeter (Sande SDC 501, China). Furthermore, the composition analysis of oil products was conducted with a gas chromatography-mass spectrometer (GC-MS, Agilent 7000B).

The output per unit, yield of pyrolysis products and the recovery rate of pyrolysis oil were calculated according to the following equations:

$$P_i = \frac{M_i}{M_{OS}} \tag{2}$$

$$Y_i = \frac{P_i}{1000} \times 100\% \tag{3}$$

$$R_{oil} = \frac{Y_{oil}}{C_{oil}} \times 100\% \tag{4}$$

where, P_i is the output per unit of pyrolysis products, g/kg; M_i is the volume of pyrolysis products, g; M_{OS} is the mass of oily sludge, kg; Y_i is the yield of pyrolysis products; i represents the char, gas and oil; R_{oil} is the recovery rate of pyrolysis oil; Y_{oil} is the yield of pyrolysis oil; C_{oil} is the oil content of oily sludge.

2.5.2 Particulate matter analyses

After the end of the experiment, the gas filtration membrane was taken out of the gas particle filter. Furthermore, pyrolysis oil was passed through the oil filtration membrane. After that, the oil and gas filtration membrane were rinsed with CH_2Cl_2 continuously until the filtrate was clarified. The oil and gas filtration membrane were dried in the oven at 105 ^{o}C and weighed after cooling. The weight of particles in the pyrolysis gas or oil is weight difference before and after use of gas or oil filter membrane.

The content of particulate matter in pyrolysis gas can be expressed as:

$$C_{gas-PM} = \frac{M_{gas-PM}}{V_{gas}} \tag{5}$$

where, $C_{gas\text{-}PM}$ is the content of particulate matter in pyrolysis gas, mg/L; $M_{gas\text{-}PM}$ is the mass of particulate matter on the gas filtration membrane, mg; V_{gas} is the volume of the pyrolysis gas, L.

The content of particulate matter in pyrolysis oil can be expressed as:

$$C_{oil-PM} = \frac{M_{oil-PM}}{V_{oil}} \tag{6}$$

where, $C_{oil\text{-}PM}$ is the content of particulate matter in pyrolysis oil, mg/kg; $M_{oil\text{-}PM}$ is the mass of particulate matter on the oil filtration membrane, mg; V_{oil} is the volume of the pyrolysis oil, L.

The analysis of particle size and surface morphology of particulate matter was done by SEM. The XRF (Axios PW4400, Holland) was used to measure the elemental composition of particulate matter.

3. Results and Discussion

3.1 TG analysis of oily sludge pyrolysis

TG and DTG curves are the change curve of oily sludge mass and oily sludge weight loss rate with temperature, respectively. Figure S1 shows the TG and DTG curves of oily sludge pyrolysis at different heating rates. TG and DTG curves show similar trends at different heating rates. The DTG curves are shifted towards the high temperature region with the increase of heating rate from 5 to 20 °C/min. Furthermore, the peak value of DTG curve increases with the increase of the heating rate. The reason is that the high heating rate leads to the increase of the pyrolysis rate of oily sludge.

The pyrolysis process can be divided into three regions according to the DTG curves. In the first region (from room temperature to 105 ^{o}C), 4.88-5.80 wt% of original weight is lost. It can be expected that the weight loss is due to the evaporation of water. The most abundant release of volatile matter (H_2, CO, CO_2, alkanes, alkenes and aromatic hydrocarbon) is observed in the temperature range 105-550 ^{o}C, which is related to volatilization and decomposition of complex organic components [24, 25]. The last weight loss (550-780^{o}C) is attributed to the decomposition of organic residues and inorganic matter such as heavy metal salts [26].

The activation energy of oily sludge pyrolysis is presented in Table S1. Coats-Redfern integral method is used to calculate the activation energy (*E*) of oily sludge pyrolysis. The activation energy of different heating rate has little difference, and increases with the increase of temperature. It can be known from Table S1 that the activation energies of three temperature ranges of oily sludge pyrolysis are 5.42-7.45, 16.09-22.03 and 35.17-68.54 kJ/mol, respectively.

3.2 Influence of the Ni-CM on gas production

The yield of each component in pyrolysis gas, and gas yield in E1 (with no CM), E2 (with blank CM) and E3 (with Ni-CM) are shown in Figure 2. Compared with the blank experiment E1, the pyrolysis gas yield of E2 increased slightly, and the distribution of H_2, CO, CO_2 and C_1~C_3 is similar to gas component of E1. The residence time of pyrolysis gas prolonged after the ceramic membrane was placed in the catalytic filter reactor, thus improving the gas reforming effect. Moreover, the blank ceramic membrane had a little catalytic activity for pyrolysis gas reforming. The existence of few active components (i.e. Fe_2O_3, NiO) can strengthen the reforming of pyrolysis gas.

The yield of pyrolysis gas is 31.46 L/kg in the E3. The total volume of gas product and H_2 concentration are significantly enhanced due to the effect of Ni-CM catalyst. The total volume of gas with Ni-CM catalyst increases to almost 2 times of the other tests (E1 and E2). Compared with pure CM (E2), the H_2 yield increased from 10.16 to 24.40 L/kg with Ni-CM catalyst (E3). In addition, the C_1-C_3 yield decreased significantly due to the high catalytic activity of Ni-CM catalyst on the pyrolysis gas reforming. Ni catalyst can promote the fracture of C-C and C-H of macromolecular long-chain aliphatic hydrocarbon in pyrolysis gas, and produce small molecular hydrocarbons such as C_1-C_3 and H_2 [27, 28].

The lower heating value (LHV) of the pyrolysis gas in E1, E2 and E3 was calculated in this study. The LHV of the pyrolysis gas in the E1, E2 and E3 is 23.53, 23.76 and 14.44 MJ/Nm^3, respectively. This phenomenon in the LHV can be ascribed to the high content C_1-C_3 of pyrolysis gas in E1 and E2.

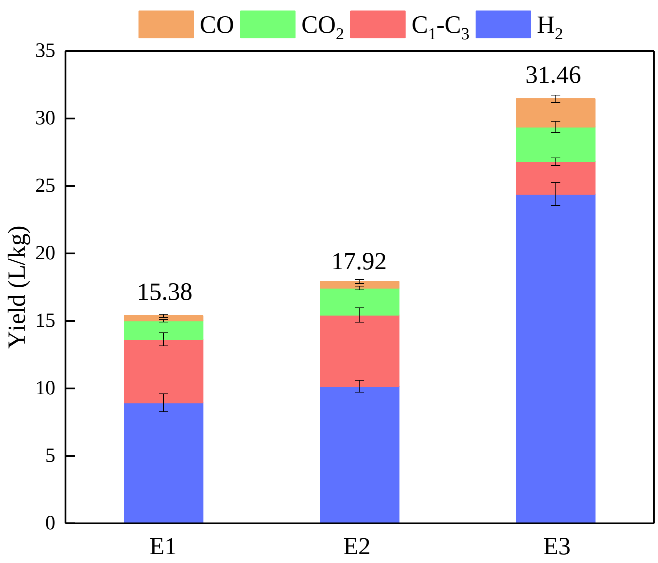

Figure 2. The yields of the pyrolysis gas, H_2, CO, CO_2 and $C_{1\sim}C_3$

Figure 3 shows the appearance and SEM images of three gas filtration membranes of E1, E2 and E3, respectively. Three points a, b and c on the filter membranes were selected for SEM analysis. It can be found that more black particles deposited on E1 filtration filter membrane, which were produced without ceramic membrane. It can be seen from the SEM image that more amorphous particles deposited on the fibers of the E1 filter membrane. While there were no obvious solid particles depositing on E2 and E3 filter membrane. It might be attributed to the filtering effect of ceramic membranes in E2 and E3 test.

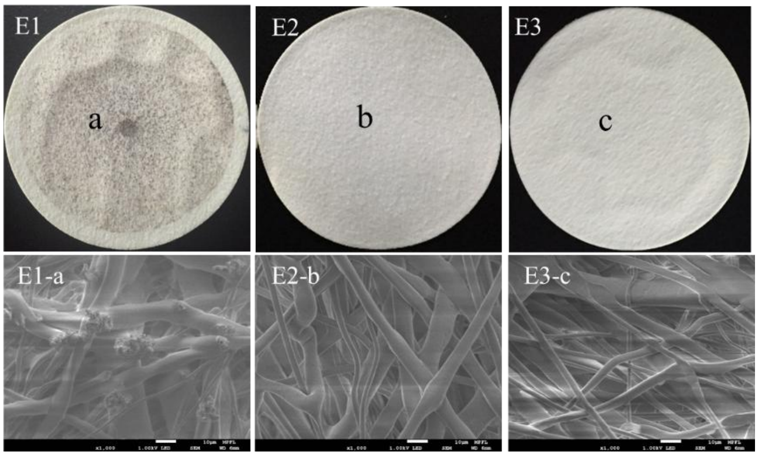

Figure 3. The filtration membrane for particles in pyrolysis gas and the SEM image

The particulate matter content of the pyrolysis gas is listed in Table 2. The particulate matter content in E1, E2 and E3 are 2.74 ± 0.29, 0.17 ± 0.05 and 0.07 ± 0.02 mg/L, respectively. It can be known that ceramic membrane has an effective filtering effect on particulate matter in gas. The main elements of particulate matter were Si, Ca, Al, Mg, Na etc (as shown in Table S2).

Table 2 The particulate matter content of the pyrolysis gas

	E1	E2	E3
$C_{gas\text{-}PM}$ (mg/L)	2.74 ± 0.29	0.17 ± 0.05	0.07 ± 0.02

3.3 Influence of the Ni-CM on oil production

The unit yield, recovery rate and HHV of the oil produced in the E1, E2 and E3 are summarized in the Table 3. The oil recovery rate of E1, E2 and E3 are 72.50 ± 1.86, 62.63 ± 0.85 and 48.21 ± 1.27%, respectively. It means that the Ni-CM catalyst can well promoted thermal cracking of sample in the E3 experiment. The secondary reaction of degassing is converted into hydrogen with a smaller molecular weight and non-condensable, and C_1-C_3. The HHV of E2 and E3 oil are 37.14 and 37.78 MJ/kg, respectively. The HHV of E1 oil is lowest due to the existence of solid particles.

Table 3 The yield, recovery rate and HHV of pyrolysis oil

	Unit yield (g/kg)	Recovery rate (%)	HHV (MJ/kg)
E1	129.72 ± 3.35	72.50 ± 1.86	35.15
E2	112.04 ± 1.52	62.63 ± 0.85	37.14
E3	86.24 ± 2.26	48.21 ± 1.27	37.78

As for the chemical components, the oil was analyzed by the GC-MS. The main identified components of the extracted oil and the pyrolysis oils (E1, E2 and E3) are shown in Figure 4. The hydrocarbons in the oil could be divided into straight-chain alkanes, branched alkanes, cyclic hydrocarbons, straight-chain alkenes, aromatic hydrocarbons and others. The dominant ones of the extracted oil are straight-chain alkanes and branched alkanes while the rest are cyclic hydrocarbons, straight-chain alkenes and aromatic hydrocarbons in small proportion. It has been proven that the pyrolysis oils have higher composition of branched alkanes, cyclic hydrocarbons, straight-chain alkenes and aromatic hydrocarbons compounds compared to extracted oil. Straight-chain alkenes were converted into other products such as cyclic hydrocarbons, straight-chain alkanes and aromatic hydrocarbons by chain breaking, dehydrogenation and isomerization during the pyrolysis process [29, 30]. The contents of branched alkanes, cyclic hydrocarbons, straight-chain alkenes, aromatic hydrocarbons of E1 oil is lower than that of E2 oil. It has been proven that the ceramic membrane plays an important role to promote oily sludge pyrolysis reaction. The content of branched alkanes, cyclic hydrocarbons, straight-chain alkenes and aromatic hydrocarbons in E3 is higher than that in E2, which indicates that the nickel catalyst can promote the conversion of alkanes [31].

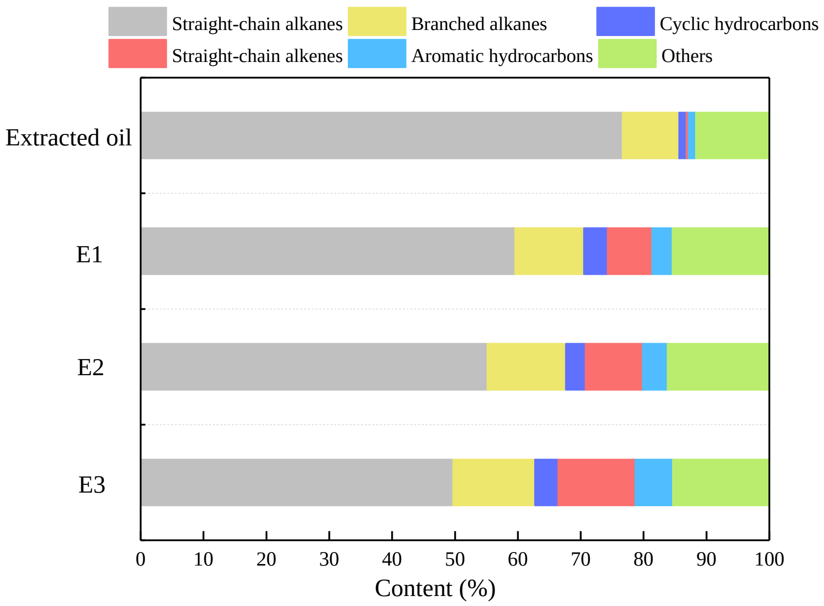

Figure 4. The analysis results of GC-MS of oil products

The oil of E1 (without CM), E2 (with blank CM) and E3 (with Ni-CM), and their high-magnification micrographs are shown in Figure 5. The pyrolysis oil produced in E1 was black and turbid. It can be seen from its high-magnification micrographs that some solid particles are mixed in the oil. The oil of E2 and E3 are clear, transparent and brown, and there are no obvious particles in their micrographs. The oil mixtures were filtered using 0.5μm pore size filter film to filter the particulate matter. The appearance and SEM images of three filtration membranes of E1, E2 and E3 oil are also presented in Figure 5. More black solid particles deposited on E1 filtration filter membrane, which were produced without ceramic membrane. It can be seen that more amorphous solid particles deposited on the fibers of the E1 filter membrane. While there are no obvious black solid particles depositing on E2 and E3 filter membrane. It can be seen that a small layer of black solid particles is trapped on the E1 filter, however, there are no obvious black solid particles on the E3 filter. Taking SEM analysis of a, b and c points on the filter membrane, it can be found that many irregular solid small particles are attached to the E1 filter fiber, the particles are adhered together, and there is agglomeration. Furthermore, the E2 and E3 filter fibers are adhesion of some solid particles less than 5 μm on the other surface. It is further demonstrated that the ceramic membrane can effectively retain solid particles having a particle size greater than 5 μm in the pyrolysis oil [32].

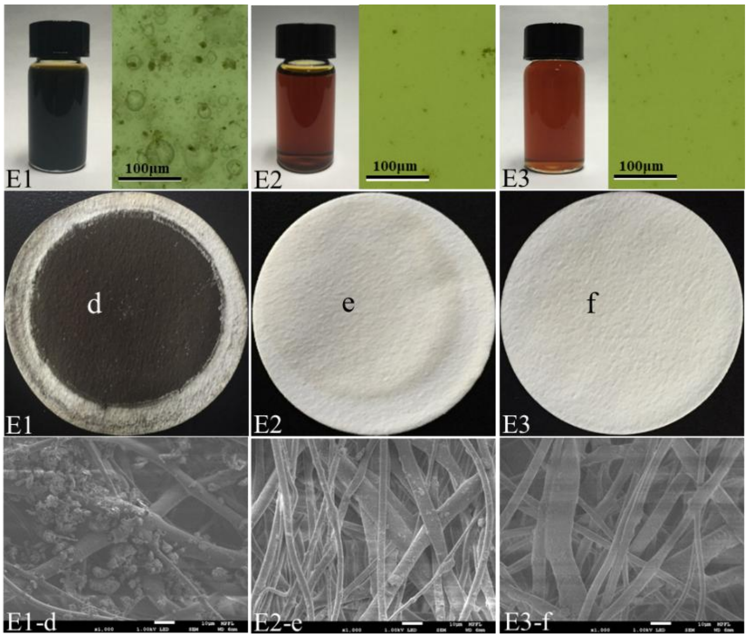

Figure 5. The images of oil samples and the particulate matter in oils

The particulate matter content of the pyrolysis oil is listed in Table 4. The particulate matter content in E1, E2 and E3 are 3708.9 ± 90.3, 234.6 ± 13.5 and 156.7 ± 8.2 mg/L, respectively. The results indicate that the ceramic membrane has a great removal effect on solid particles. The XRF was used to determine the element content of particulate matter (as shown in Table S3). The main elements of particulate matter were Si, Ca, Al, Mg, Na etc, and amounts of trace heavy metal elements: Cr (978 mg/kg), Mn (929 mg/kg), Ni (495 mg/kg), Cu (143 mg/kg) and Zn (88 mg/kg).

Table 4 The particulate matter content of pyrolysis oil

	E1	E2	E3
$C_{oil\text{-}PM}$ (mg/L)	3708.9 ± 90.3	234.6 ± 13.5	156.7 ± 8.2

3.4 Life time analysis of catalyst

The stability of Ni-CM catalyst was tested during the long-time pyrolysis of oily sludge in the same reactor. The lifetime experiment (E4) was carried out at same experimental conditions (i.e. pyrolysis temperature of 500 ^oC and feeding rate of 4.17 g/min). Each gas bag was responsible for an hour to collect the pyrolysis gas. In Figure 6, it can be observed that the H_2 yield decreased from 80.16% to 43.26% when the reaction time is below 420 min, while the content of C_1~C_3 increased from 6.42% at 60 min to 44.18% at 420 min. The content of H_2 and C_1~C_3 tend to be stable and fluctuated around 45.00% when the reaction time was higher than 420 min. The content of CO was decreased during the whole pyrolysis process, while the CO_2 content fluctuated and remained at about 3.00% after 420 min. The effective use time of Ni-CM catalyst was 420 min in the oily sludge catalytic pyrolysis experiment. With the increase of experimental time, coke deposits on the catalyst surface to decrease the catalytic activity.

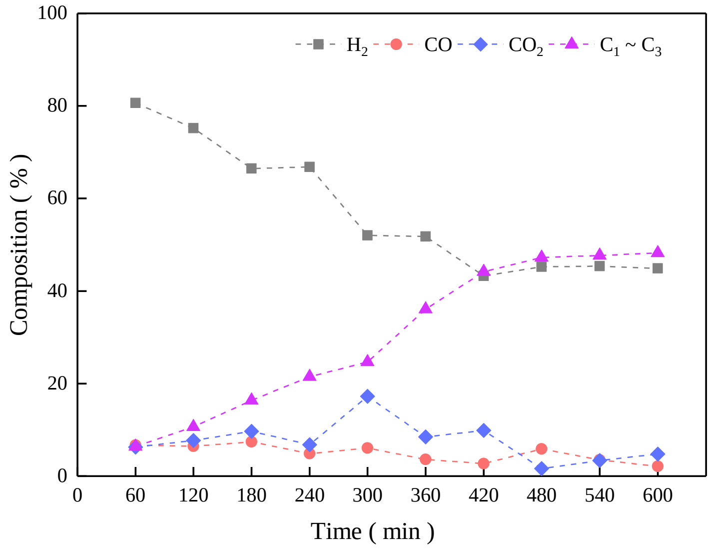

Figure 6. Influence of reaction time on the composition of the pyrolysis gas

3.5 Characterizations of fresh and used catalysts

The SEM images of CM, fresh Ni-CM and used E4-Ni-CM with different magnification times of 1000 and 30000 are presented in Figure 7. It can be seen that the surface of blank CM is smooth, the surface of fresh Ni-CM was covered by a layer of Ni particles, while more amorphous carbon deposited on used E4-Ni-CM catalyst from the 1000-fold SEM images. It can be seen from the 30000-fold SEM image of fresh Ni-CM catalyst that Ni particle (<100 nm) is uniformly distributed on the ceramic membrane's surface. In Figure 8, the surface of E4-Ni-CM is almost completely covered with carbon, and no Ni particles were observed on E4-Ni-CM catalyst. It is indicated that the Ni-CM catalyst could not play its catalytic role and promote the secondary reforming of pyrolysis gas.

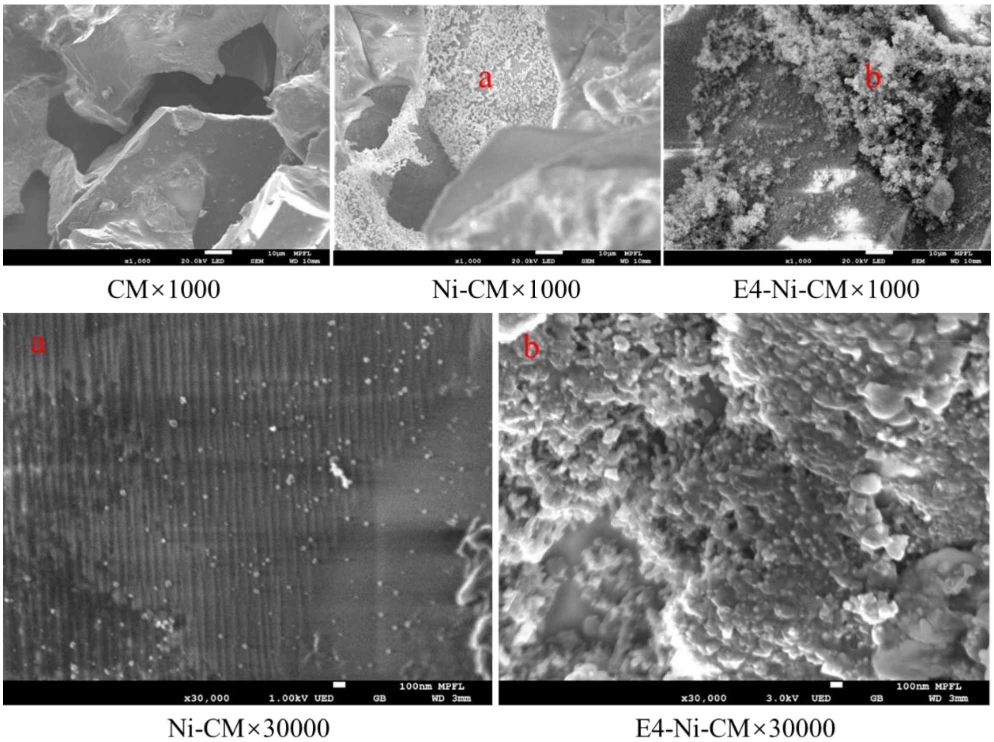

Figure 7. The SEM images of CM, Ni-CM, and E4-Ni-CM

BSE is an electron imaging technique based on SEM, which can reflect the element distribution on the sample surface. EDS technique is employed to show the Ni, Si and Al element distribution on the surface and inside of fresh catalyst. The SEM-BSE images with EDS mapping of surface and inside of fresh Ni-CM and used E4-Ni-CM were presented in Figure S2 and Figure S3, respectively. It can be seen that a large number of Ni particles are clustered in white spots on the BSE image. Mass of Ni particles are also scattered inside the fresh Ni-CM. For used catalyst shown in Figure S3, less aluminum indicates that the carbon completely deposited on the surface of ceramic membrane. A large amount of carbon was accumulated in the space inside E4-Ni-CM, and Ni particles were detected at the space of carbon accumulation, as shown in Figure S3.

XRF analysis results of blank CM, fresh Ni-CM catalyst and E4-Ni-CM catalyst are shown in Table S4. Based on the elemental composition, it is observed that both blank CM, fresh Ni-CM catalyst and E4-Ni-CM catalyst have a high content of Si (28%) and Al (>11%). Some metals such as Na, Ti, K, Mg, Ca, Fe, Zr, Sr, Cr, and Mn are also detected in the ceramic membrane. The contents of nickel are about 1.96% and 1.64% in the fresh Ni-CM and used E4-Ni-CM, respectively. This decrease of nickel content is mainly due to the coverage of carbon on used E4-Ni-CM catalyst.

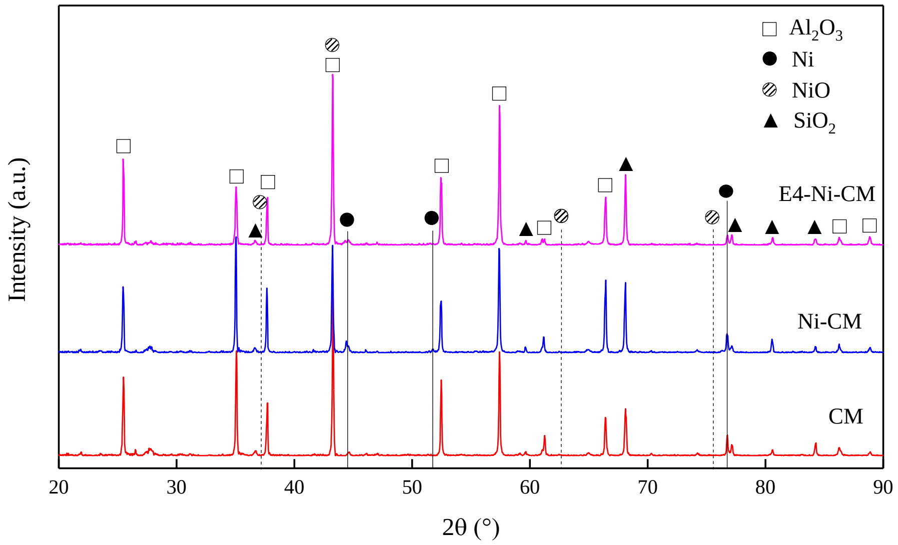

Figure 8. The XRD patterns of CM, Ni-CM, E4-Ni-CM.

Figure 8 presents the XRD patterns of blank CM, fresh Ni-CM and used E4-Ni-CM catalysts. Al_2O_3 is the main component of ceramic membrane and its characteristic peaks are: 2θ = 25.46°, 35.06°, 37.73°, 43.24°, 52.47°, 57.42°, 60.61°, 66.44°, 76.77°, 86.26° and 88.83°. Furthermore, the diffraction peaks of SiO_2 (2θ = 36.56°, 59.95°, 68.12°, 77.65°, 80.04° and 84.95°) are also found in the figure. It is verified that SiO_2 is one of the main components of ceramic membrane. The characteristic peaks of Ni (2θ = 44.41°, 51.77°, 76.33°) are detected which illustrates the presence of Ni in fresh Ni-CM and used E4-Ni-CM. Moreover, it is noticeable that no peaks of NiO appear on the curves. It indicates that Ni on fresh Ni-CM and used Ni-CM exists in the form of active single substance. The deactivation of Ni-CM catalyst is due to the fact that the surface of the Ni-CM catalyst is almost completely covered by carbon during the oily sludge pyrolysis process [33].

4. Conclusion

Ni-ceramic membrane catalyst was prepared by impregnation method and characterized in this study. The clean catalytic pyrolysis of oily sludge was carried out on the spiral reactor to study the effect of ceramic membrane on oily sludge pyrolysis and particulate removal. It was found that the Ni loading on the ceramic membrane could improve the yield of the pyrolysis gas. The yield of the pyrolysis gas produced from the reaction with Ni-ceramic membrane was 31.46 L/kg, while the recovery rate of pyrolysis oil was 48.21%. On the contrary, the yield of the pyrolysis gas produced from the reaction with clean ceramic membrane was 17.92 L/kg, while the recovery rate of pyrolysis oil was 62.63%. The results indicate that the ceramic membrane has a great removal effect on solid particles from pyrolysis products. In addition, a long-time catalytic pyrolysis experiment was carried out. With the feeding speed of 4.17 g/min and reaction temperature of 500^{o}C, the Ni-ceramic membrane could be used continuously for 420 min. As a result, Ni-ceramic membrane catalyst can be used for the pyrolysis of oily sludge.

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